One-dimensionality in glassy carbon

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(Received 21 January 1983; revised manuscript received 2 May 1983)

A negative $T^{-1/2}$ dependence of a component of the electrical conductivity, indicative of one-dimensional transport, was found in glassy carbon heat treated at temperatures less than 2200 °C. The microstructure, as examined in lattice images in the transmission electron microscope, the Porod-law dependence obtained in small-angle scattering, and the decrease in the d_{002}-spacing interlayer as measured by x-ray diffraction (above this critical temperature) support this thesis.

There has been increased interest in the electrical conductivity of solids restricted to less than three dimensions, as in thin wires,[1-6] thin sheets[7] such as MOSFET (metal-oxide-semiconductor field-effect transistor) channels,[8-10] and some organometallic materials.[11,12] We believe that we have found an example of one-dimensional conductivity in glassy carbon. Our results empirically agree with theory and the case of one-dimensionality is supported by the observed microstructure.

Glassy carbon,[13] a prototype nongraphitizing bulk carbon, is prepared by thermally decomposing a thermosetting resin, typically a mixture of phenol formaldehyde and furfuryl alcohol. The as received material has been given a final 1-h processing at 1000 °C in inert atmosphere. It was heat treated further for 3 h in a graphite furnace under an inert gas at temperatures ranging from 1200 to 2700 °C. Specimens were ground, polished to uniform thickness, and ultrasonically cut into a four-probe bar configuration. Electrical conductivity measurements were made under isothermal conditions at temperatures from 3 to 300 K.

The results can be divided into two classes according to the behavior of the low-temperature conductivity. For high heat treatment temperatures, greater than about 2200 °C, the conductivity decreases with temperature to a shallow minimum [Fig. 1(a)]. Of more interest in this Brief Report, for low heat treatment temperatures the conductivity continues to decrease more rapidly with decreasing temperature, as shown in Fig. 1(b).

Saxena and Bragg[14] were the first to formulate an empirical expression for the electrical conductivity of glassy carbon in the heat treatment temperature range of interest. In the present study,[15] the conductivity σ as a function of measurement temperature T is written as

$$\sigma = A + B\exp(-CT^{-1/4}) - DT^{-1/2} ,$$

where the first term is attributed to strongly scattering metallic conductivity independent of temperature and the second term to variable range hopping. Both terms have no strong dependence on the heat treatment temperature. The last and new term is a low-temperature correction term to the metallic conductivity and, as shown in Fig. 2, is only important for heat treatment temperatures less than about 2200 °C.

Kaveh and Mott[16] have reviewed two approaches to a correction of the metallic conductivity. They are the localization approach by Abrahams *et al.*[17] and the electron interaction approach by Altshuler, Aronov, and Lee.[18] In the localization approach, the carrier is allowed to diffuse until an inelastic scattering event takes place (trapping by a localized state), and thus diffusion of the carriers is limited by the inelastic scattering time. In the electron interaction approach, the effective number of carriers is affected by the correlation between the shift of potential energy and the broadening of the momentum distribution of the carriers themselves as scaled by the physical dimensions. Both mechanisms may be operating simultaneously.

The interaction approach has been used to predict a correction in one dimension

$$\delta\sigma = -\frac{e^2}{\hbar}\left(\frac{2}{\pi}\right)^2\frac{1}{A}\left(\frac{\hbar D}{kT}\right)^{1/2} ,$$

where D is a diffusion coefficient related to the mean free path and A is the cross-sectional area. Such a $-T^{-1/2}$ dependence for a component of the electrical conductivity indicates the possibility of one-dimensional transport in glassy carbon. To examine the plausibility of this thesis, the microstructure is briefly reviewed to establish that glassy carbon is a highly interconnected network of filaments or laths on a minute scale.

The microstructure of glass carbon is descended from that

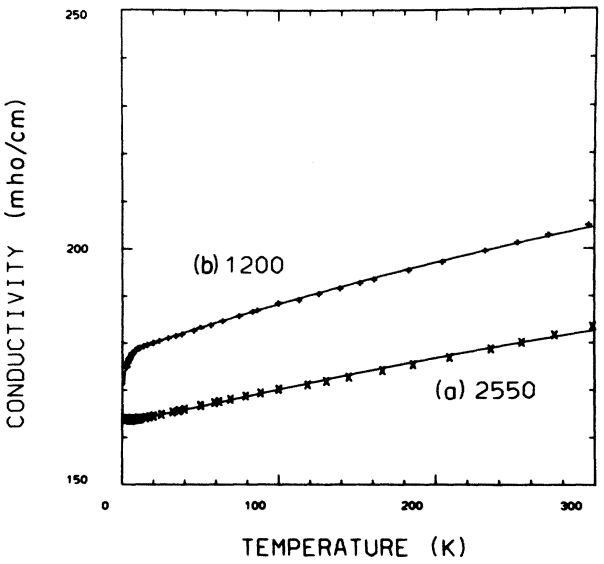


FIG. 1. Electrical conductivity of glassy carbon heat treated at (a) 2550 and (b) 1200 °C. The solid lines are calculated fitted lines from the empirical equation $\sigma = A + B\exp(-CT^{-1/4}) - DT^{-1/2}$.

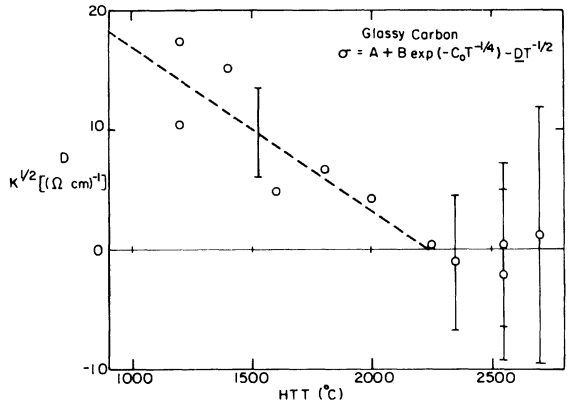


FIG. 2. One-dimensional electrical conductivity component parameter D of glassy carbon as a function of heat treatment temperature (HTT).

of its polymer precursors. X-ray diffraction line profiles for glassy carbon are extremely diffuse, yielding only the 002, *hk* band and 004 peaks associated with turbostratic carbons and are dominated by small angle scattering. Studies[19-22] show that the apparent crystallite dimensions in the basal plane and normal to it increase with heat treatment temperature and time from about 34 and 12 Å, respectively, for the as-received material, but corrections for strain and other factors are expected to increase these values substantially.[19,20,23] Also, the interlayer spacing for the 002 plane remains constant at 3.44 Å and does not begin to decrease toward the 3.35 Å of graphite until temperatures above 2000 °C are reached.[19,24]

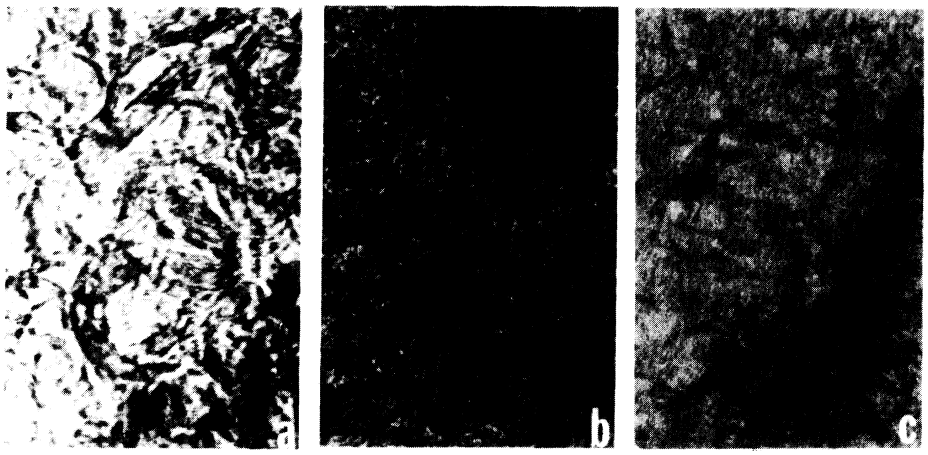
Small-angle scattering in glassy carbon is so large due to the very large number of very small microvoids (33 vol.%) that it has been adopted as a standard calibration material for small-angle scattering apparatuses.[25] These voids have been analyzed through the use of the Guinier approximation[26] to yield radii of gyration in the range of 5–20 Å (Refs. 27–30) depending upon heat treatment temperature and time. The Porod law[31] is obeyed in glassy carbon heat treated above about 2000 °C, that is, the intensity at relatively large scattering vectors ($h = 4\pi \sin\theta/\lambda$) is proportional to h^{-4}. The specific surface area of glassy carbon has been determined by this method to be 700–1100 m^2/cm^3, again as a function of heat treatment temperature and time.[27,28,30] In glassy carbon heat treated below 2000 °C, a positive deviation from the Porod law is observed and becomes greater for lower heat treatment temperatures.[27,28] These positive deviations have a number of causes, among them anisotropic density fluctuations within the scattering medium,[32] and have been detected in a number of carbons and polymers.[33-37]

The microstructure, as lattice imaged in transmission electron microscopy using (002) planes, is shown in Fig. 3 for a representative set of heat treatment temperatures. For 2700 °C [Fig. 3(a)], ribbons or laths of the order of 15 planes thick (50 Å) and greater than 170 Å long are imaged. In Fig. 3(b), for 2250 °C material, the laths are only about a third as coarse. Figure 3(c) is an image of 1800 °C glassy carbon, where only the beginnings of the coherent lath structure observed for higher temperatures are present. The "amorphous" phase perhaps suggests linear fibers, but no conclusions can be made about its structure, except that its features are probably finer than for any of the laths observed. Attempts to lattice image lower-temperature heat treated glassy carbon failed due to lack of contrast and coherence.

Other changes are that the weight loss during heat treatment about 2000 °C becomes constant ($\simeq 1$ wt.%) (Ref. 38) and that the Hall effect becomes positive.[15]

Low-temperature heat treated glassy carbon is a labyrinth of carbon chains or ribbons of near polymeric chain dimensions, which would mean a few tens of square angstroms cross section and several tens or hundreds of angstroms between crosslinks. Consequently, evaluation of a single filament in this highly interconnected network is difficult, even if any confluence or filament proximity effects are ignored. The assumption was made that in this complex heterogeneous material the temperature dependence of a component of the electrical conductivity should be reflected in a simple parallel element expression.

The relevant length for the localization approach is the inelastic scattering length. From the strongly scattering metallic term of the electrical conductivity,[15] the mean free path has been estimated to be 15 Å, and should be approxi-



(a) (b) (c)

FIG. 3. Transmission electron microscope 002 lattice images under identical conditions of glassy carbon heated at (a) 2700, (b) 2250, and (c) 1800°C. The fringes imaged have a 3.4-Å spacing. The microscope work is by courtesy of Dr. Ron Gronsky.

mately the inelastic scattering length. As shown above, this length is about the scale of the width of the polymer chain.

The relevant length for the interaction model is the coherent scattering length $(\hbar D/kT)^{1/2}$. If the diffusion time can be calculated from the drift mobility $(e\tau/m_{\text{eff}})$ which is assumed to be approximately the Hall mobility (0.002 $m^2/V\,sec$),[15] then the diffusion constant $D(l^2/\tau)$ is 3×10^{-3} m^2/sec, and the coherent scattering length is 1.6×10^{-7} $m\,K^{1/2}/T^{1/2}$. If the area of the filaments is liberally taken to be 400 $Å^2$, then the coarsely calculated effect is a few orders of magnitude larger than observed.

In summary, the microstructure of glassy carbon heat treated below about 2200 °C is best described as tightly interwound laths which do not possess sufficient registry to produce coherent lattice images. This scale is minute enough to admit the possibility of a one-dimensional correction to the metallic electrical conductivity having the observed $-T^{-1/2}$ dependence. The nature of the transition to the semicoherent laths imaged in the transmission electron microscope has not been fully established.

The implications of this work are that one-dimensional effects could exist in a bulk network of filaments. Furthermore, such effects may be found in other carbonized polymers processed above the nonmetal-metal transition temperature (about 700 °C for glassy carbon) and in carbon fibers.

ACKNOWLEDGMENTS

We gratefully acknowledge Dr. Ron Gronsky for his lattice imaging work and Dr. A. S. Rao for preparation of the microscope specimens. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

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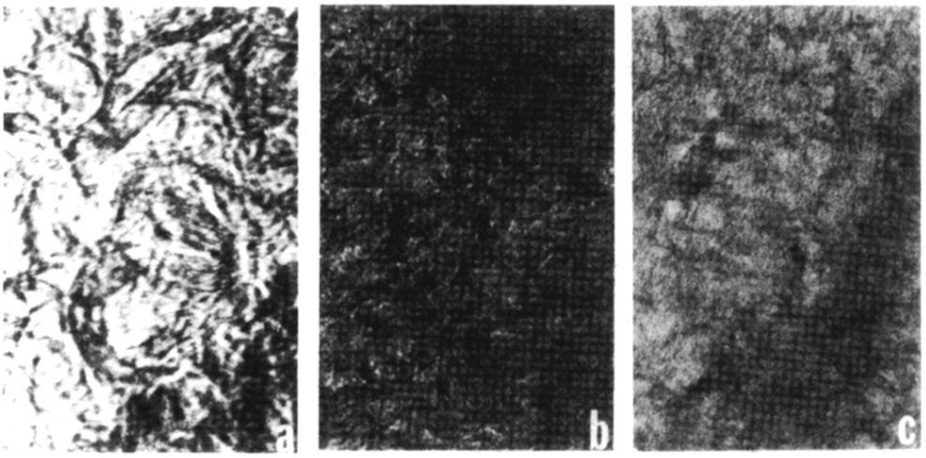

(a) (b) (c)

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